DETERMINATION OF THE STRUCTURE OF META-DINITROBENZENE BY PATTERSON FOURIER SUMMATION *

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ABSTRACT. The structure of meta-dinitrobenzene has been studied by the Patterson Fourier Summation Method. Relative values of the integrated intensities of reflections from the hko planes have been measured from Weissenberg goniometer photographs by the help of a Zeiss microphotometer. By using needle shaped crystals much elongated along the c-axis, a single traversal of the scanning spot of light was found necessary and a considerable economy of labour was thus effected. The absolute intensities were obtained by comparison with reflections from rocksalt in a powder photograph of a mixture of known proportion of metadinitrobenzene and rock-salt. From the projections on the (001) plane of the different interatomic vectors in the unit cell obtained by Patterson Analysis a preliminary determination of the atomic arrangements has been made.

INTRODUCTION

Meta-dinitrobenzene crystallises in the orthorhombic bipyramidal class.[1] The space-group has been determined independently by Hertel and Schneider[2] and by Hendricks.[3] They found that this crystal belongs to the space-group D_{2h}^{16}Pbnm with a unit cell containing 4 molecules having dimensions $a_0 = 13.3$ Å, $b_0 = 14.2$ Å, $c_0 = 3.82$ Å. Thus it was concluded that the molecule had a plane of symmetry parallel to the 001 plane and as the dimension of the c axis is very short the plane of symmetry must be along the benzene ring. This is very unusual for the benzene rings in aromatic compounds. Because none of the aromatic compounds that have been so far studied except this one show a plane of symmetry along the plane of the benzene ring. Further N—O bonds must either lie parallel to the benzene plane or lie symmetrically on the two sides of the N atom in a plane perpendicular to the molecular plane. The former alterna-

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tive is ruled out as it was shown by Hendricks [3] that it is impossible thereby to explain the intensities of the ool planes. As regards the N-O bonds in para-dinitrobenzene, there is however, a controversy[4] as regards whether the bonds are symmetrical about N, but here the two bonds come out to be symmetrical as a consequence of the space-group. Thus it is very useful to see whether these bonds are similar or not to the N-O bonds in the para-compound. In order to decide this point as well as to determine the structure of a benzene ring having a plane of symmetry along the plane of the ring, a complete analysis of the structure of this compound has been taken up. A projection on the ool face should show all the different atoms separated out except that the two oxygen atoms attached to a single nitrogen atom will be superposed on each other. So this projection will give us practically the complete structure.

An attempt at determining the x and y co-ordinates of the atoms by a trial and error method proved unsuccessful due to the number of unknown parameters as well as the uncertainties about the atomic structure factors of oxygen and nitrogen. So a Patterson analysis of this projection has been presented in this paper.

EXPERIMENTAL

Meta-dinitrobenzene was crystallised from absolute alcohol. Long, very narrow needle-shaped crystals were obtained, c-axes of which are parallel to the lengths of the crystals. This shape has an advantage in measuring the intensities, as we may consider the intensity of a diffraction spot to be uniform over its length. Such a crystal was mounted on the Weissenberg goniometer with the c-axis along the axis of rotation and at the initial position the x-ray beam was made parallel to the a-axis. These adjustments were made with the help of a Czapski two-circle goniometer. Copper Kα radiation was used. The spots were indexed by the help of charts prepared according to Wooster and Wooster's [5] method. Intensities of the spots were measured with the help of a Zeiss microphotometer, by allowing the scanning light to traverse across the centre of the spots. The photometer records were converted to intensities by the help of a standard wedge obtained in the manner of Robinson.[6] Intensity curves were thus obtained from the photometer curves by point to point plotting and the relative values of integrated intensity were determined by finding the areas under the intensity curves.

For measurements of the absolute intensities a powder photograph was taken with a stick prepared with known proportions of meta-dinitrobenzene and rock-salt. The lines (130) and (310) due to the former could be identified uniquely and were well separated from the nearest lines. The integrated intensities of these lines were compared with the (200) and (220) lines of rock-salt. From the

known structure factors of rock-salt the structure factors for these two reflections could be calculated according to the relation

$$\frac{I_m}{I_r}=\frac{\left(\frac{1}{abc}\right)^2 p_m \cdot F_m^2 \cdot \frac{m_m}{\rho_m} \cdot \frac{1+\cos^2 2\theta_m}{\sin 2\theta_m \cdot \sin\theta_m}}{\left(\frac{1}{a_0^3}\right)^2 \cdot p_r \cdot F_r^2 \cdot \frac{m_r}{\rho_r} \cdot \frac{1+\cos^2 2\theta_r}{\sin 2\theta_r \cdot \sin\theta_r}}$$

where $\frac{I_m}{I_r}$ is the ratio of the integrated intensities of the meta-dinitrobenzene line and rock-salt line measured from the powder photograph. a, b, c are the cell dimensions of meta-dinitrobenzene and a_0 is the length of the unit cell of rock-salt. $\frac{m_m}{m_r}$ is the ratio of the masses of the two substances taken in the powder stick.

p = number of equivalent planes.

F = structure factor.

ρ = density.

θ = glancing angle and the subscripts m and r refer to metadinitrobenzene and rock-salt respectively.

The values of the structure factors of (130) and (310) planes thus obtained were utilised in determining the absolute values of the structure factors of all other planes from the relative measurements. The values of the structure factors obtained thus are given in Table I.

TABLE I

Plane	Structure factor	Plane	Structure factor
040	46·3	370	29.0
060	56.7	400	57.2
080	37.0	420	44.2
0(12)0	27.7	430	22.1
120	43.5	450	30.5
130	67·7	510	34.9
140	56.0	520	58.3
160	33.8	530	27.6
210	42.0	540	25.0
220	35.0	560	34.3
230	45.7	570	33.9
240	26.8	580	29.2
250	40.1	600	70.4
270	27.5	620	29.2
310	72.9	710	60.2
330	44.3	720	30.7
340	25.9	800	19.3
350	26·7	(10)00	26.2
360	69.1	—	—

For the Patterson summation a quarter of the cell is taken so that $a/2$ and $b/2$ are the sides. The whole cell can be obtained from this by the appli-

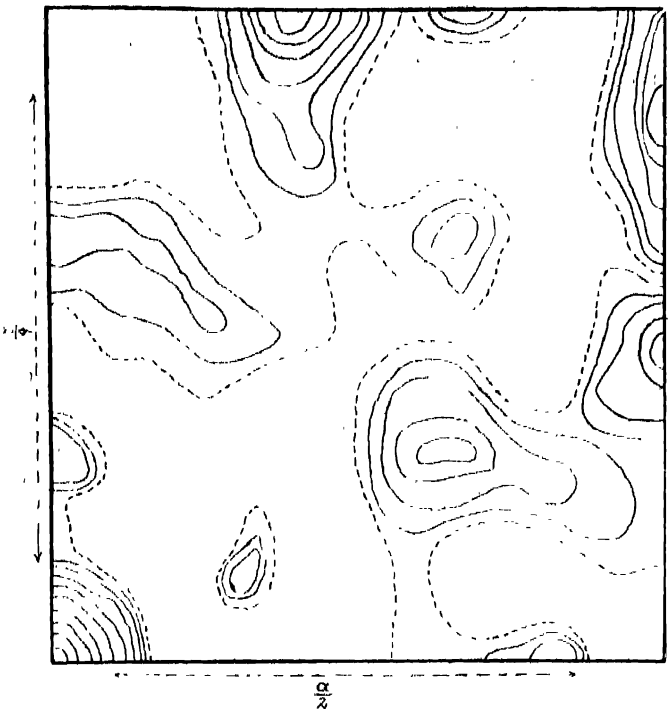

FIGURE 1

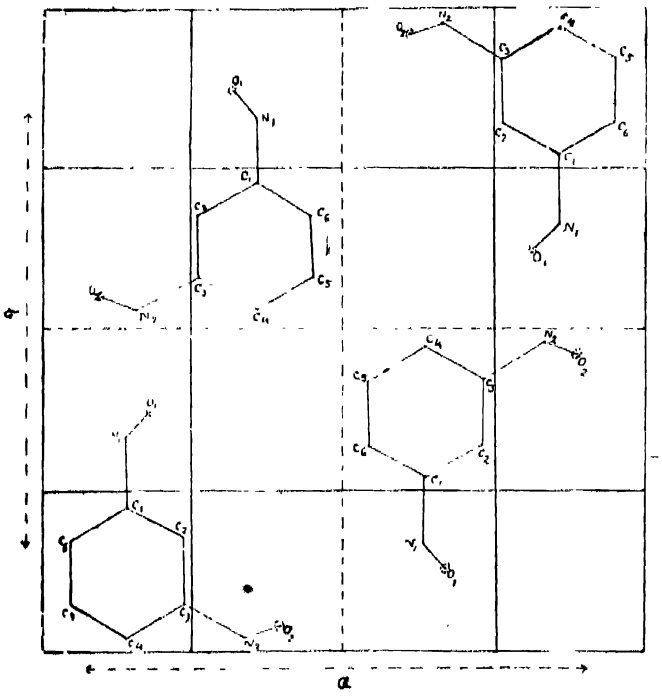

FIGURE 2

cation of the planes of symmetry. Each side was divided into sub-divisions of $a/24$, and $b/24$ and the Patterson densities were calculated according to

$$A_{(x,y)} = \sum_{h=o}^{h=e} \sum_{k=-a}^{k=a} F^2_{(hko)} \cdot e^{2\pi i\left(\frac{hx}{a} + \frac{ky}{b}\right.}$$

where A (x, y) is the Patterson sum at the point x, y. By plotting these Patterson sums lines are drawn through points of equal density and are shown in Figure 1.

The peaks of the diagram are then correlated with the different interatomic vectors and the magnitudes of these vectors with their inclinations with the x-axis obtained in this way are given in Table II, the symbols for the different atoms used in this table will be understood from a reference to Figure 2 where is given the arrangement of the meta-dinitrobenzene molecule in the unit cell as can explain these interatomic vectors:

TABLE II

Interatomic Distance Vectors

[Each of O_1 and O_2 represents the projections of two oxygen atoms]

Atomic pair	Interatomic distance	Angle with 'a' axis
$C_{1a}O_{1a}$; $C_{1d}O_{1d}$	2.2Å	79°
$C_{3c}O_{2c}$; $C_{3b}O_{2b}$	2.2Å	25°
$C_{1a}N_{1a}$; $C_{1b}N_{1b}$; $C_{1c}N_{1c}$; $C_{1d}N_{1d}$	4.3Å	90°
$C_{6b}N_{2b}$; $C_{6c}N_{2c}$	4.3Å	30°
$C_{4a}O_{1a}$; $C_{4d}O_{1d}$	4.8Å	84°
$C_{6b}O_{1b}$; $C_{6c}O_{2c}$	4.8Å	24°
$C_{1a}C_{1b}$; $C_{2a}C_{6b}$; $C_{3a}C_{5b}$; $C_{4a}C_{4b}$; $C_{5a}C_{3b}$; $C_{6a}C_{2b}$; $N_{1a}N_{2b}$; $C_{1c}C_{1d}$; $C_{2c}C_{6d}$; $C_{3c}C_{5d}$; $C_{4c}C_{4d}$; $C_{5c}C_{3d}$; $C_{6c}C_{2d}$; $N_{1c}N_{2d}$	7.5Å	70°
$C_{1a}C_{4c}$; $C_{2a}C_{3c}$; $C_{1a}C_{2c}$; $C_{4a}C_{1c}$; $C_{5a}C_{6c}$; $C_{1b}C_{4d}$; $C_{2b}C_{3d}$; $C_{6a}C_{5a}$; $C_{1b}C_{2d}$; $C_{4b}C_{1d}$; $C_{5b}C_{6d}$; $C_{6b}C_{5d}$	7.5Å	27°
$O_{1a}O_{2c}$; $O_{1b}O_{2d}$	4.3Å	22°
$N_{1a}C_{5c}$; $N_{1b}C_{3d}$; $C_{1a}C_{6c}$; $C_{1b}C_{2d}$	5.6Å	17°
$C_{4a}C_{4c}$; $C_{4b}C_{4d}$; $N_{2a}N_{2c}$; $N_{2b}N_{2c}$	8.9Å	41°
$N_{1b}C_{3d}$; $N_{1a}C_{6c}$; $N_{1d}C_{6b}$; $N_{1c}C_{2a}$	5.4Å	2°
$N_{1a}C_{6b}$; $N_{2d}C_{6c}$	6.3Å	48°
$N_{1a}C_{3b}$; $N_{1d}C_{3c}$	4.0Å	66°
$C_{2c}O_{1d}$; $O_{1a}C_{2b}$	4.5Å	75°

The atomic parameters are deduced as an approximation from this structure and are given in Table III.

TABLE III

Atomic parameters

Atom	x/a	y/b
C_1	0.146	0.224
C_2	0.237	0.174
C_3	0.237	0.076
C_4	0.146	0.0264
C_5	0.055	0.076
C_6	0.055	0.174
N_1	0.146	0.329
N_2	0.303	0.023
O_1	0.172	0.372
O_2	0.386	0.033

Fourier projections on the three crystallographic planes are being attempted on the basis of this result.

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